

d 2 ab

63-3414

L4: 2 of 2

ABSTRACT:

PURPOSE: To form an **amorphous silicon** film having a sufficient **deposition rate** and excellent electric characteristics by a method wherein a thermal CVD method is performed at the substrate temperature of 480.degree.C or below using trisilane or higher **silanes**.

CONSTITUTION: The substrate 4 consisting of a wafer and the like is inserted into the chamber 1 consisting of a heating means 2, a susceptor 3, a gas blow-out hole 5, the exhaust hole and the like connected to a gas exhaust means 7, they are placed on the upper surface of the susceptor 3. When they are heated up to 400.degree.C or thereabout by a heating means 2, the **silane** of high order which is higher than trisilane is introduced into the chamber 1. As a result, an **amorphous silicon** film is formed on

63-3414

L4: 2 of 2

the surface of the substrate 4 by thermal decomposition reaction. At this time, atmospheric gas is introduced into the chamber 1 in advance, and after the temperature of the substrate 4 has been stabilized, raw gas is introduced, and the temperature variation when a film is formed can be made small substantially by performing a thermal CVD.

=>

(19) Office of Patents, Government of Japan (JP)
(11) Patent Application Kokai (Laid Open) No. Sho 63-3414

(12) Kokai Patent KOho (Publication) (A)

(51) Int. Cl.⁴ H 01 L 21/205, //H 01 L 29/78

Identification Code: 3 1 1

Intra-Office Coordination Nos. 7739-5F, F-8422-5F

(43) Kokai Date: January 8, 1988

Request for Examination: Yes

Number of Inventions: One

(Total number of Pages - Six)

--

(54) Name of the Invention: Process for Preparing Silicon Film

(21) Patent Application No. Sho 61-147380

(22) Date of Application: June 24, 1986

(72) Inventor: Yutaka Hayashi, c/o Institute of Industrial Technology,
Comprehensive Electron Technology Laboratory, 1-4, 1-chome, Umezono,
Sakura Mura, Shinji Gun, Ibaragi Ken

(72) Inventor: Mitsuyuki Nakayama, c/o Institute of Industrial Technology,
Comprehensive Electron Technology Laboratory, 1-4, 1-chome, Umezono,
Sakura Mura, Shinji Gun, Ibaragi Ken

(71) Applicant: Industrial Technology Institute (Kogyo Gijutsu In), 3-1, 1-
chome, Kasumigaseki, Chiyoda Ku, Tokyo.

(74) Agent: Tsutomu Mogami, patent attorney, and one other

(71) Applicant: Shinetsu Kagaku Kogyo Kabushiki Kaisha (Shinetsu Chemical
Industry Company, Limited), 6-1, 2-chome, Ohte Machi, Chiyoda Ku, Tokyo

(71) Applicant: Seiko Denshi Kogyo Kabushiki Kaisha (Seiko Electronic Indus-
try Company, Limited), 31-1, 6-chome, Kamedo, Koto Ku, Tokyo

(74) Tsutomu Mogami, patent attorney, and one other (Continued to the past
page).

--

Specification

1. Name of the Invention: Process for Preparing Silicon Film

2. Scope of Claims for Patent:

(1) A process for the preparation of a silicon film, characterized in
that a silane which is higher than trisilane (Si_3H_8) in degree is sent

--

as a material into a chamber in a device wherein a gas exhaust means and gas supply means are connected to the chamber that accommodates a substrate heating means and the silicon film is grown by heated CVD at a substrate temperature of 480 degrees centigrade or lower by maintaining the temperature of the wall surface of the said chamber lower than the heated CVD.

(2) A process for the preparation of silicon films as described in Claim 1 of the Scope of Claims for Patent, characterized in that the atmospheric gas (H_2 , N_2 , He , Ar , etc.) is introduced into the aforementioned chamber beforehand and, after the substrate temperature has been set, the material gas is introduced and the silicon film is grown.

(Field of Industrial Utilization)

This invention relates to a process for the preparation of a silicon film to be used in a thin-film transistor, etc. without showing much change due to the passage of time.

(Outline of the Invention)

This invention is for the production of a stable amorphous silicon film of high crystallinity by means of a heated CVD employing a silane which is higher than trisilane in degree.

(Technology According to Prior Art)

Heated CVD is used in the preparation of silicon films which are not damaged by such charged electron particles as plasma, etc.

If, in the case where a hydrogenated amorphous silicon film is prepared by the heated CVD method, a monosilane (SiH_4) is used as the gas material, it is necessary to raise the substrate temperature to the range between 600 and 650 degrees centigrade and, the amount of the bound hydrogen that compensates the structural defect in the film is extremely small, with a result that the properties of the film are low according to the technology of prior art. A report has been published by Yoshinori Ashida, et al. to the effect that, in the case where disilane (Si_2H_6) is employed, an amorphous silicon film containing a suitable degree of hydrogen can be formed. (Refer to Yoshinori Ashida, Yasuyoshi Nishida, Masataka Hirose, Yukio, Osaka and Kenichi Kojima, J. J. Appl. Phys. 23 (1984), 129).

Heretofore-known heated CVD process using disilane as has been practiced in the past employs a reaction device of the hot wall type, wherein even the chamber is heated in addition to the heating of the substrate. In the hot wall type reaction device, impurities on the inner wall of the chamber are easily taken into the silicon film, with a consequence that it is difficult to improve the quality of the film. In addition, there is a problem in that the silicon particles increase on the surface of the substrate because of the gaseous phase reaction with a result that the surface tends to become rough.

Meanwhile, there is a problem in that the deposition rate is low in the reaction device of the cold wall type that heats only the substrate without heating the chamber.

Accordingly, the purpose of this invention lies in forming an amorphous silicon film which has a sufficient deposition rate at a low substrate temperature and which has satisfactory electric properties and remains stable even in the reaction device of the cold wall type.

(Means for Solving the Problem)

In this invention, the problem has been solved by clarifying the relationship between the film-making conditions in the hot CVD and the properties of the silicon film by using a silane whose degree is higher than the trisilane as the material.

(Function)

Since the reactivity of a silane whose degree is higher than trisilane is high as compared with disilane, there is obtained a satisfactory deposition rate and it becomes possible to maximize such film-making conditions as the substrate temperature and the reaction pressure, etc. that are related to the quality of the film.

(Example)

First, the examples of the device to be used in this invention will be explained by referring to Figures 1 (a) and (b).

In Figure 1(a), code 1 indicates a chamber which has such a substrate heating means 2 as a heater, etc. A susceptor 3 whose heat conductivity is high is fixed and heating is carried out. Such a substrate 4 as a quartz plate, a glass plate, a stainless steel plate, a silicon wafer, etc. is placed on the susceptor 3. (In the case where it is facing downward, a metal fastener, etc. is used for fixing same.) A gas blow-out part 5 is formed in the neighborhood of the substrate 4 and a gas exhaust means 3 (Translator's Note: 3 is unclear; it may be 5), is connected with the chamber 1 in the gas supply means 6 and the chamber 1.

The system ranging from the gas supply means 6 to the gas blow-out part has its temperature maintained above the boiling point of the gas material (which is 53.1 degrees centigrade in the case of trisilane). In addition, a vacuum gauge and an observation window, etc. are provided, if necessary, on the side of the chamber 1, and an air-cooling or water-cooling pipe for cooling purposes is connected to same.

In Figure 1(b), lamp heating is used for the means 2 for heating the substrate, where the chamber 1 is made of quartz whose light absorption is small and the susceptor 3 is made of carbon, etc. whose light absorption is large.

If, by using such a device, the substrate is heated to a temperature in the neighborhood of 400 degrees centigrade and a silane whose degree is higher than trisilane is introduced into the chamber, an amorphous silicon film can be formed on the surface of the substrate 4 because of the heat decomposition reaction. In this case, the temperature on the side wall of the chamber 1 is in the neighborhood of 200 degrees centigrade. When it is to be further cooled, it is only necessary to blow the air or N₂ gas, etc. to the chamber 1.

Detailed conditions for deposition will be shown below:

Figure 2 shows an example of the data pertaining to the deposition rate of the amorphous film to the surface of a quartz substrate by using 100 per cent trisilane. In Figure 3, the axis of abscissas indicates the reciprocal number of the substrate temperature T_{sub} and the axis of ordinates indicates the rate of deposition ($(\lambda)/\text{min.}$). The Δ , \square , \circ , \diamond and ∇ marks indicate the cases where the reaction pressures are one, two, five, 10 and 12 Torr. respectively. There is a deposition rate of 60 (λ)/min. at 10 Torr and at the temperature of 420 degrees centigrade and this is a value which is sufficient for the production of a semiconductor element.

In the case where dilution was carried out by using such atmospheric gas as (Translator's Note: Unclear but they look like H_2 , N_2 , He, Ar, etc) the deposition was such that the rate was approximately the same, provided that the pressure of the trisilane is the same as the reaction pressure shown in Figure 3.

Figure 3 shows an example of the dependency of the optical band gap and the amount of the combined hydrogen in the case where the reaction pressure is five Torr by using a 100 per cent trisilane. When the substrate temperature is below 480 degrees centigrade, the optical band gap is approximately 1.65 eV and the amount of the united hydrogen is approximately 7.5 per cent, where they are approximately constant.

When the substrate temperature exceeds 480 degrees centigrade, both the optical band gap and the combined hydrogen amount are reduced. It has been thus learned that hydrogen dissociation takes place when the substrate temperature exceeds 480 degrees centigrade in the hot CVD using a silane whose degree is higher than trisilane.

Figure 4 shows the dependency of the dark conductivity indicated by a black circle in the case where the reaction pressure using a 100 per cent trisilane is five Torr and the photoconductivity which is indicated by a white circle under a beam application of AMI spectrum 60 m W/cm^2 upon the temperature of the substrate. Even though the photoconductivity is not high, the ratio between the photoconductivity and the dark conductivity is more than three digits. At a temperature of the substrate higher than 480 degrees centigrade, further, both the photoconductivity and the dark conductivity come down by the dissociation of hydrogen.

Figure 5 shows an example of the infra-red absorption characteristics. Ordinarily, an elongation and contraction vibration of a SiH union having a peak in the neighborhood of 2000 cm^{-1} and an elongation and contraction vibration of a SiH₂ union having a peak in the neighborhood of 2100 cm^{-1} are observed. In the case of an amorphous silicon film by the heated CVD of trisilane, the peak of SiH₂ union is scarcely observed and SiH unions are the mainstay. Thus, it can be said that the film is of high quality.

An example of the cross section of a thin film transistor prepared by utilizing the aforementioned deposition data will be shown in Figure 6.

A non-dope amorphous silicon film 8 due to the heated CVD of a silane whose order is higher than trisilane is deposited to approximately 500 angstroms on a gate 6 which has utilized a silicon substrate of the low resistance p type and a gate insulation film 7 of approximately 900 angstroms obtained by the heated oxidation of the aforementioned silicon substrate in a dry O₂ atmosphere of 1100 degrees centigrade. In addition, a source 9 and a drain 10 consisting of two layers including n- amorphous silicon layer and a metal layer such as

Ni, etc. are formed.

Figure 7 shows an example of the output characteristics of an actual thin film transistor. The gate source electric voltage was changed in 2V steps to the range between 20 and 30 volts and the ratio between the channel width W and the channel length L or W/L is 40. In the case where the source drain voltage is "wiped in" from zero to 10 volts and then to zero volt, the histerisis is extremely small and stable. The ON/OFF electric current ratio of this thin film transistor is more than six digits and the threshold value voltage and the electron motion degree as obtained from the saturation range were satisfactory at 18 volts and $0.1 \text{ cm}^2/\text{V.S.}$ respectively.

The change of the drain electric current in terms of the time elapsed is shown in Figure 8 in comparison with a thin film transistor prepared by the plasma CVD of a monosilane. The plasma CVD sample was prepared into a film by using the same chamber as the heated CVD at a substrate temperature of 300 degrees centigrade under a reaction pressure of 0.7 Torr with a high frequency electric power of 10 watts.

The axis of abscissas indicates the time elapsed after the impression of a bias required for flowing the drain electric current by one $(\mu)\text{A.}$ and the axis of ordinates indicates the ratio of the value I_d at each time against the initial value $I_d(0)$ of the drain electric current in Figure 9, where the solid line indicates the case of a thin film transistor by the plasma CVD and the broken line indicates the case of a thin film transistor by the heated CVD. In the case of the thin film transistor by the heated CVD, the time change of the drain electric current is small and stable as compared with the case involving the plasma CVD.

Figures 9 (a) and (b) show an example of the order of the actual depositions, where the axis of abscissas indicates the time and the axis of ordinates indicates both the chamber pressure and the substrate temperature.

Figure 9 (a) shows the case of 100 per cent trisilane. When a trisilane is introduced into the vacuated chamber 1, deposition starts. At this juncture, if the chamber pressure suddenly increases, the heat conductance between the substrate heating means 2 and the susceptor 3 and between the susceptor 3 and the substrate 4 is improved, with a result that the temperature of the substrate rises by as much as 20 degrees centigrade.

After a short while, temperature control follows and the temperature of the substrate is stabilized. When the chamber pressure is higher than 10 Torrs, this phenomenon becomes conspicuous. The substrate temperature variations at the time of the initiation of this deposition lowers the control of the film thickness and the uniformity of the film quality in the case where the deposition time is short.

If, therefore, 10 or more Torrs of a diluted gas such as H_2 , N_2 , He and Ar, etc. is introduced into the chamber beforehand and the trisilane is introduced after the substrate temperature has been stabilized, the variation in the substrate temperature can be controlled to less than one degrees centigrade, with a result that it becomes possible to carry out stable deposition. This stabilization effect was also observed under a chamber pressure in the neighborhood of five Torrs.

(Effect of the Invention)

As has been explained above in detail, this invention has the advantage of obtaining a stable amorphous silicon film whose electric characteristics are satisfactory in the

case where the heated CVD is carried out at a substrate temperature of 480 degrees centigrade or lower by using a silane whose order is higher than trisilane.

If heated CVD is carried out after introducing an atmospheric gas into the chamber, thereby stabilizing the temperature of the substrate, and after introducing the gas material, the substrate temperature change at the time of film-making can be made extremely small.

In view of the fact that it is a process using a low temperature and without any damage to the charged particles, moreover, it is obvious that it will have no adverse effect upon the other elements that have already been formed even in the case where it is combined with such a process as LSI, etc.

4. Concise Explanation of the Drawings:

Figure 1(a) is a rough cross section of a device using a heater according to this invention. Figure 1(b) is a rough cross section of a device using a lamp for heating according to this invention. Figure 2 shows the dependency upon the substrate temperature of the deposition rate of the heated CVD employing 100 per cent trisilane according to this invention.

Figure 3 shows the dependency on the substrate temperature of the optical band gap and hydrogen content of this invention. Figure 4 shows the dependency of the electroconductivity of this invention upon the substrate temperature. Figure 5 is an infra-red absorption characteristic figure of the silicon film according to this invention.

Figure 6 is a cross section of the thin film transistor prepared by using the data shown in Figures 2 through 5. Figure 7 shows the output characteristics of the thin film transistor shown in Figure 6.

Figure 8 likewise shows the change of the drain electric current in terms of time elapsed. Figure 9(a) shows an example of the procedures of the deposition in the case where 100 per cent trisilane is employed. Figure 9(b) shows an example of the procedures of the deposition in the case where dilution was similarly carried out by using an atmospheric gas.

In the above drawings, code 1 indicates a chamber, 2 is a substrate heating means, 3 is a susceptor, 4 is a substrate, 5 is a gas blow-out part, 6 is a gas supply means, 7 is an exhaust means, 8 is a silicon film, 9 is a source, and 10 is a drain.

- End -

Applicant: President, Institute of Industrial Technology
Shinetsu Chemical Industry Company, Limited
Seiko Electronics Industry Company, Limited

Designated Agent: Kohei Sato, Director, Electronic Technology Comprehensive Research Laboratory,
Institute of Industrial Technology

Sub-agent: Tsutomu Mogami, patent attorney (and one other) (seal)

--
(Insert Figure 1(a), p. 64. Cross section of the manufacturing device. 1. Chamber. 2. Substrate heating means. 3. Susceptor. 4. Substrate. 5. Gas blow-out part. 6. Gas supply means. 7. Exhaust means.)

(Insert Figure 1(b), p. 64. Cross section of the manufacturing device. The codes are the same as in Figure 1(a).)

(Insert Figure 2 on p. 64. Dependency of the deposition rate upon the substrate temperature. a. Deposition rate. b.

Substrate temperature (deg. C.).)

(Insert Figure 3 on p. 65. Dependency of the optical band gap and the amount of united hydrogen upon the substrate temperature. a. Amount of united hydrogen (per cent). b. Optical band gap (eV). c. Substrate temperature.)

(Insert Figure 4 on p. 65. Dependency of electroconductivity upon the substrate temperature. a. Conductivity. b. Substrate temperature. (deg. C.).)

(Insert Figure 5 on p. 65. Infra-red absorption characteristics. a. Rate of absorption. (cm^{-1}). b. Number of waves (cm^{-1}).)

(Insert Figure 6 on p. 65. Cross section of the thin film transistor. 6. Gate. 7. Gate insulating film. 8. Silicon film. 9. Source. 10. Drain.)

(Insert Figure 7 on p. 65. Output characteristics of the thin film transistor. a. Drain electric current. b. Drain-source voltage.)

(Insert Figure 8 on p. 66. Change of the drain electric current in terms of time elapsed. a. Bias impression time (hour).)

(Insert Figure 9(a) on p. 66. An example of the procedures of the deposition. a. Substrate temperature. b. Chamber pressure (Torr). c. Time (minute). d. Vacuation. e. Trisilane introduction. f. Vacuation.)

(Insert Figure 9(b) on p. 66. An example of the procedures of the deposition. a. Substrate temperature (deg. C.). b. Chamber pressure (Torr). c. Time (minute). d. Introduction of diluted gas. e. Introduction of trisilane. f. Vacuation.)

(Continued from the first page)

(72) Inventor: Mitsuo Umemura, c/o Shinetsu Chemical Industry

- Company, Limited, Silicon Electronic Material Technical
Laboratory, 13-1, 2-chome, Isobe, Yasunaka Shi, Gumma Ken
- (72) Inventor: Tomo Okazaki, c/o Shinetsu Chemical Industry Company,
Limited, Silicon Electronic Material Technology Research
Laboratory, 13-1, 2-chome, Isobe, Yasunaka Shi, Gumma Ken
- (72) Inventor: Ryoji Takada, c/o Seiko Electronics Industry
Company, Limited, 31-1, 6-chome, Kame do, Koto Ku, Tokyo
- (72) Inventor: Masaaki Kamiya, c/o Seiko Electronics Industry
Company, Limited, 31-1, 6-chome, Kamedo, Koto Ku, Tokyo